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Enhancement of up-conversion efficiency by combining rare earth-doped phosphors with PbS quantum dots

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Abstract

This paper aims to enhance the up-conversion phenomena observed in silicon solar cells by combining a rare earth-doped phosphor with PbS quantum dots. Two different ways of adhering the up-converter and the fluorescent material to a bifacial solar cell are implemented: dissolving the powder in a spin-on oxide and by dissolving it in a silicone gel. Characterization is carried out through photocurrent and photoluminescence measurements. The improvement in photocurrent detected by the combination of the up-converter and the PbS quantum dots is 60% better than without them, demonstrating that the absorption and emission characteristics of the quantum dots embedded both in the oxide or the silicone can be tuned to the desired spectral region.

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1. Introduction

Photon converters can enhance the performance of solar cells as they have the ability to condition the solar spectrum, thus suiting the semiconductor bandgap better. In the case of up-conversion (UC), advantage can be taken of the transmitted energy [1]. The implementation and characterization of up-converters (UC) layers on the rear of bifacial silicon solar cells (BSSC) has been reported by several authors [2] [3]. Pan et al. [4] attached some commercial phosphors to the BSSC by dissolving them either in a spin-on oxide or a silicone. The performance was characterized through External Quantum Efficiency (EQE) measurements, demonstrating a gain in photocurrent in the IR wavelength range. This gain is quite small, firstly because response of the UC process is greatly dependent on light intensity, and also because the wavelength range in which it takes place is very narrow, corresponding to a small absorption range of the rare-earth dopant. The use of photoluminescence materials to enhance the UC phenomena has been suggested a number of times for photovoltaic applications [5] [6] [7]. The idea is to widen the

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IR light being used through a material that can absorb it in a range of wavelengths where the UC does not respond, and re-emit it in the wavelengths where it does respond.

The UC used in the experiments reported is called PTIR545/F, made by the company *Phosphor Technology*. PTIR545/F is a very fine pink powder that seems to consist, according to EDX measurements, of ZnSO_4 doped with ytterbium (Yb) and a small fraction of erbium (Er). This commercial phosphor is typically sold for applications in IR leds, printing inks, credit cards, etc. It can be excited in the 1500 nm range and re-emits it in shorter wavelengths, mainly in the 500 nm range.

PbS quantum dots (QDs) have appropriate absorption and emission properties for combination with the UC and the BSSC, and are readily commercially available. There are several requirements of the QDs that have to be fulfilled for this purpose. For instance, Suyver et al. [8] reported that the diameter of the QDs should be below 30nm to reduce light scattering and for that reason a 5.3 nm diameter PbS QDs made by the company *Evident Technology* were selected and used in this work. These QDs have large quantum efficiency and high indices of refraction compared to the phosphors, which Si devices can take advantage of [9]. The energy transfer will probably occur through radiative emission from the QDs followed by absorption by the UC phosphor.

Figure 1 details the EQE as a function of wavelength for the BSSC itself, the BSSC with PTIR545/F-UC, and the absorption and emission of the *Evident Technology* PbS QDs. While the EQE for the solar cell is significant in the range 350-1100 nm, the UC layer is able to extend it (although with a very low response) in the 1488-1564 nm range. The PbS QDs have absorption precisely in the range where neither the BSSC itself nor the UC take advantage of the light (1200-1500 nm), and the emission takes place in the range where the UC is active, presenting a possible route to improve the UC efficiency.

In this paper we first present the characterization results for the BSSC with UC, discussing the influence of the light power on the UC efficiency. Second, we combine the UC with PbS QDs characterize the approach through measurements of photocurrent and photoluminescence (PL).

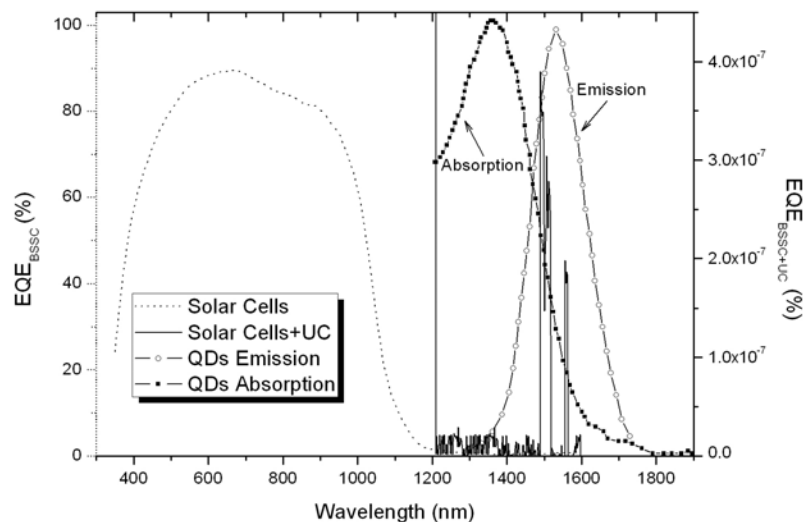


Figure 1. Experimental results of the EQE for the BSSC with a UC layer, and the emission and absorption reported for the PbS-QDs in arbitrary units.

2. Characterization of up-conversion effect under IR LED illumination

As reported in previous deliverables and publications [4] we have manufactured BSSC and attached the UC to the rear using two different methods: either by dissolving it in a spin-on oxide, or by doing so in a silicone gel. Characterization is made through EQE measurements adapted to the IR range, the light source being a quartz-tungsten-halogen (QTH) incandescent lamp (200 W). Figure 2 shows a comparison of the gain in photocurrent

experienced for the two approaches. It demonstrates that the photon conversion phenomenon takes place, although the gain in photocurrent is rather small.

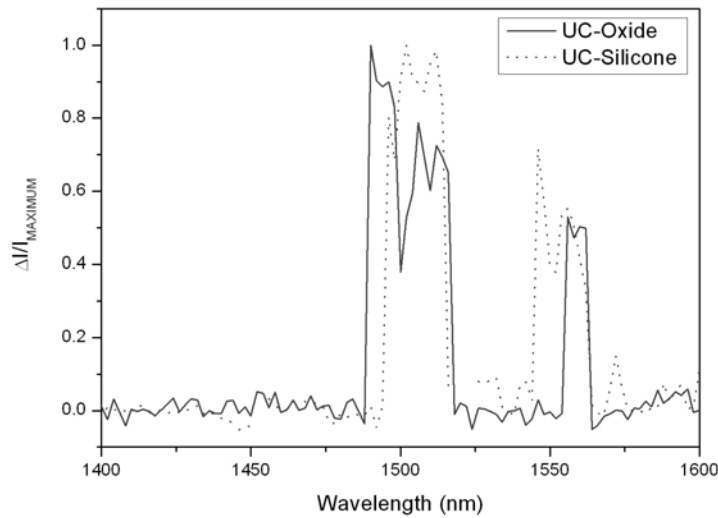


Figure 2. Normalized photocurrent for the two ways of attaching the *PTIR545/F*–UC to the BSSC dissolved in an oxide or silicone for the QTH incandescent lamp.

By translating the increase in photocurrent to EQE, we can compare the performance of the *PTIR545/F* for the two alternative binders, the oxide and silicone, with that of others reported in the literature for silicon solar cells. In Table 1 this comparison is detailed.

Table 1. Comparative EQE results with different up-converters materials.

<i>Material</i>	<i>Peak wavelength (nm)</i>	<i>Incident light power (mW)</i>	<i>Increase of the EQE (%)</i>
NaYF ₄ :Er ³⁺ [2]	1523	6	3.4
BaCl ₂ :Er ³⁺ [3]	1535	3	3.6x10 ⁻⁴
PTIR545/F-oxide	1488-1518	0.1	4.0x10 ⁻⁷
PTIR545/F-silicone	1494-1516	0.1	5.9x10 ⁻⁶

The response of the *PTIR545/F* phosphor is much lower than for the others, and this is not only related to the kind of phosphor, but also to the fact that the incident power light is much lower. The up-conversion process for Erbium-doped compounds is based on the ETU mechanisms, and its efficiency is greatly dependent on the incident power [10].

In our EQE system we are restricted to low power intensities in the IR region because our light source is optimized for the visible energy range. So, in order to increase the detectivity of the UC effect we have replaced the halogen lamp with two LEDs sources. Some of their characteristics are shown in Table 2. Although the power for the LEDs is 20 times higher than that of the QTH lamp for the wavelengths of interest, it experiences a big reduction when passing through the monochromator, so for the following measurements the monochromator has not been used. That changes the interpretation of the measurements because we lose the spectral resolution, but nevertheless gives valuable information on the enhancement of photocurrent (or not) resulting from photon conversion. Figure 3 compares the results for the characterization with the QTH lamp and with the LEDs, showing some correspondence.

The increase in photocurrent when illuminating with the LEDs is higher than for the QTH lamp, showing the influence of the incident power. In addition, having two LEDs centered in two different wavelengths (1450 nm and 1550 nm), one is able to distinguish the two peaks that this UC has in this range. On the other hand, the reduction in wavelength resolution avoids determining the width of the corresponding peaks. Furthermore, with the use of the

LED source, although incident power is still low in comparison with experiments reported in the literature, it is possible to contrast samples with a different concentration of UC, which is not possible using our QTH lamp.

Table 2. Characteristics of the IR LED lamp used in the experiments provided by the company *Roithner Lasertechnik*.

LED name	Peak Wavelength (nm)	Half Width (nm)	Maximum Radiated Power (mW)
1450-03	1450	100	2.0
1550-525	1550	100	2.0

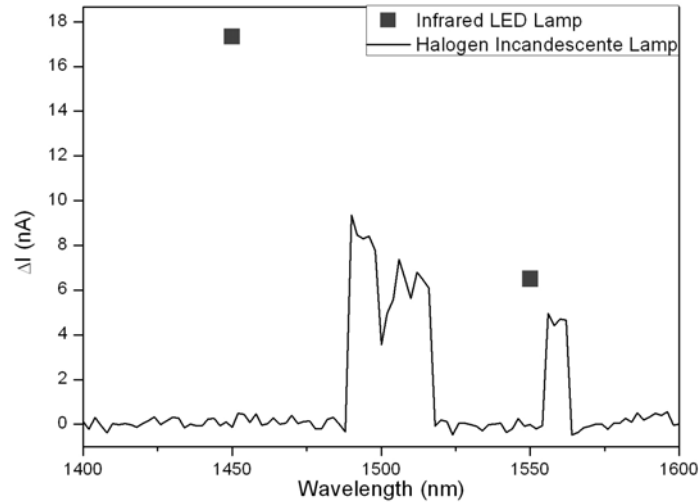


Figure 3. Increase in photocurrent versus wavelength for the PTIR545/F up-converter embedded in the spin-on oxide layer, for the different source lamps. The dots correspond to the LED sources, which are not just the response in the indicated wavelength, but in the range of the LED width shown in Table 2.

3. Enhancement of up-conversion performance by combination with quantum dots

To test the potential enhancement of PTIR545/F-UC performance with the PbS-QDs, they have been dissolved together with the UC, either in the spin-on oxide or in the silicone gel, attached to the BSSC and characterized through measurements of photocurrent and photoluminescence. We can see a schematic structure of the BSSC with UC and QDs in both deposition techniques in Figure 4.

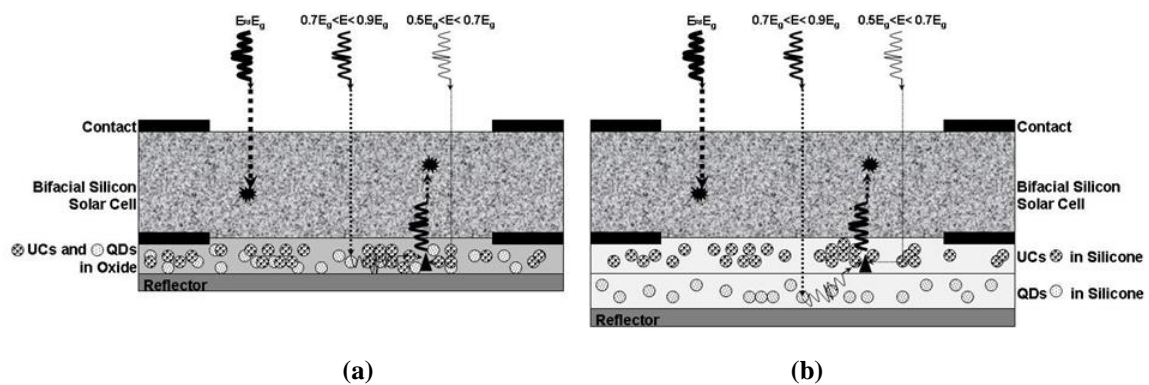


Figure 4. Schematic structure of the BSSC for the two ways of attaching the UC and QDs: by oxide (a) and silicone (b). * represents the generation of an electron-hole pair and ▲ the UC phenomena.

The increase in photocurrent for the LEDs source detected for a BSSC with UCs and QDs is shown in Figure 5 for both implementation modes, the oxide (a) and the silicone (b). The improvement in photocurrent detected for a BSSC with PTIR545/F-UC and PbS-QDs is in all cases 60% better than without them, demonstrating that the absorption and emission characteristics of the QDs embedded in oxide and silicone can be tuned to the desired spectral region. These experimental results are similar to those calculated by Löper et al. [11], where they calculated a fluorescent quantum efficiency of about 50 for commercial nanocrystals.

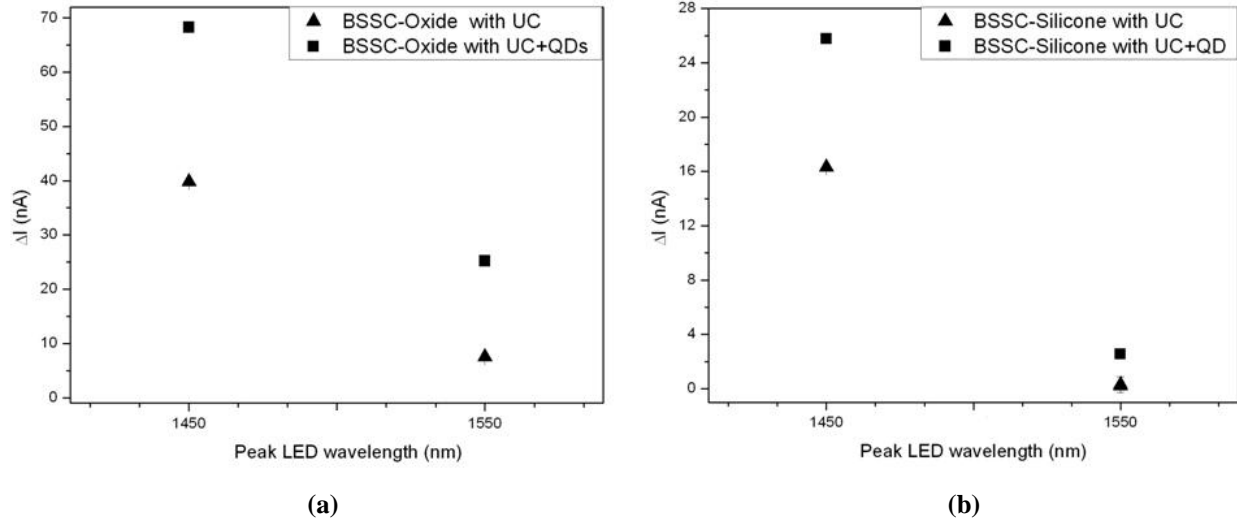


Figure 5. Increase in photocurrent versus wavelength for a BSSC with UC-PTIR545/F embedded in the oxide (a) and in the silicone (b) with and without QDs. The dots correspond to the LED sources, which are not just the response in the indicated wavelength, but in the range of the LED width shown in Table 2

To give insight into the phenomena taking place, the configuration of the Yb-Er UC system is represented in Figure 6 (a). The PL spectrum measured for the PTIR545/F-UC in silicone gel with and without QDs is also shown in Figure 6 (b). Laser excitation is at 514.5 nm, but emission in the visible light wavelength (corresponding to transitions from the levels $^4I_{9/2}$, $^4F_{9/2}$, $^4H_{11/2}$ of the Er^{3+} ion directly to the ground state) cannot be detected. As the detector covers the NIR wavelength range, only transitions in various steps to lower levels ($^4I_{11/2}$ and $^4I_{13/2}$) will leave a signature in the PL spectrum. These excited states decay to the next lower lying state or directly and radiatively to the ground state. Photons emitted by a transition process from $^4I_{11/2}$ or higher excited levels back to the ground state have more energy than the bandgap for silicon.

Three NIR infrared emissions are observed in the PL spectrum. The $^4I_{13/2} \rightarrow ^4I_{15/2}$ Er^{3+} ions transition (1520 nm) is clearly observed, independently of the presence of QDs. Furthermore, the shape of the peak agrees with experiments reported by Auzel [12]. The same intensity for both cases (with and without QDs) is the result of the much stronger concentration of the codopant Yb^{3+} ion compared to the Er^{3+} ion. Then, the increase expected from the implementation of QD is not achieved. The PL measurement also shows the strongest emission for the transition from the level $^2F_{5/2}$ back to the ground state ($^2F_{5/2} \rightarrow ^2F_{7/2}$) at the wavelength of around 980 nm because of the Yb^{3+} ions. For the excitation of this level only one photon is needed, and the absorption cross-section for the Yb^{3+} is more pronounced than Er^{3+} . Thus the overall peak is also independent of the presence of QDs, because it refers to the PTIR545/F-UC. The transition from the level $^4I_{11/2}$ back to the ground is the only one different for the case with PbS-QDs. In the transition $^4I_{11/2} \rightarrow ^4I_{15/2}$ (980 nm) for Er^{3+} ions, two photons are needed, and it is ideal to enhance the BSSC efficiency. Efficient nonradiative energy transfer from the $^4I_{11/2}$ state can be beneficial for silicon, which has a strong absorption at this energy. Furthermore, this transition can be possible because of the near-perfect resonance between the Yb^{3+} ($^2F_{5/2}$) and Er^{3+} ($^4I_{11/2}$) states, as a very efficient energy transfer from Yb^{3+} to Er^{3+} takes place only when the population of the $^2F_{5/2}$ state becomes significant [8].

Based on Figure 5 and Figure 6 (b), we conclude that the application of a layer with UC and QDs to a BSSC can enable such a solar cell to use sub-band gap light indirectly ($\lambda > 1100$ nm) that would otherwise not be absorbed by

the silicon. The emission of the PbS-QDs coincides with the ground state absorption of the Er^{3+} ($^4\text{I}_{15/2} \rightarrow ^4\text{I}_{13/2}$). Consecutive absorption as well as energy transfer-based UC processes takes place from this first excited state to a second one [12]. However, the PTIR545/F-UC is not so appropriate for solar cells, because of the combination of Yb^{3+} and Er^{3+} . The UC effect occurs because of the absorption of 980 nm-photons in Yb^{3+} , and after the de-excitation of this state, the energy is transferred to the Er^{3+} , so that it competes with silicon for the NIR photons with wavelengths of between 900 and 1100 nm [13]. But the PTIR545/F-UC has additional absorption peaks as a result of the Er^{3+} (1509, 1522, 1547, 1552 and 1600 nm), and our measurements show that they can contribute to an enhancement of photocurrent. The small broadening of the excitation spectra as compared to other up-converters used with BSSC [10] [14] can be to the result of the influence of the phonon energy of the different host materials.

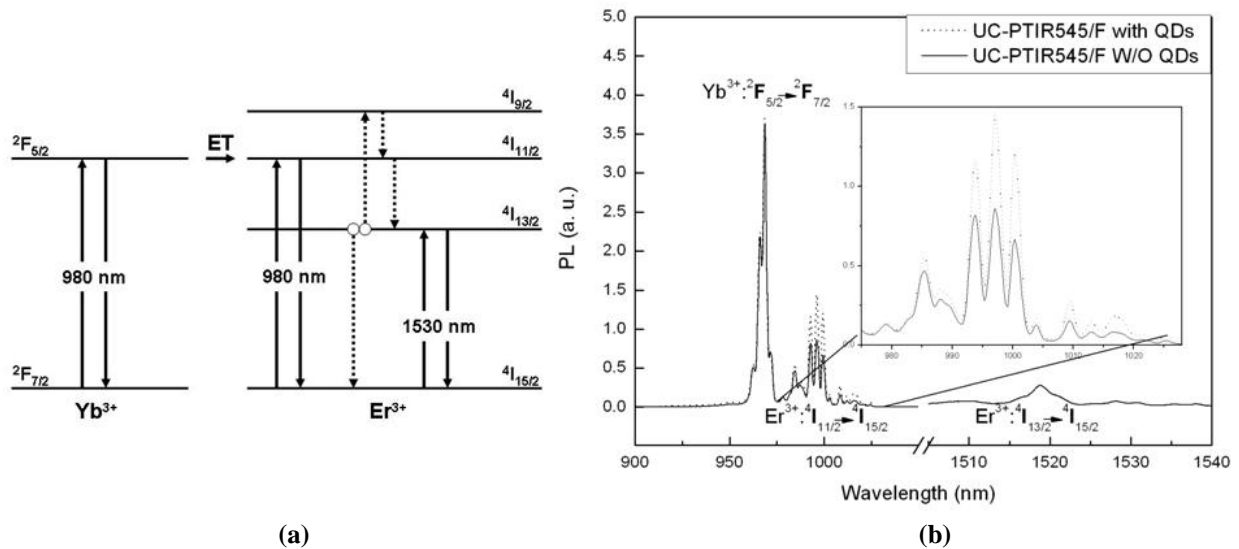


Figure 6. Schematic configuration of the Yb^{3+} - Er^{3+} UC system (a). Radiative absorption and emission are indicated by solid lines and non-radiative ones by dashed lines. The open circles show the initial state of the center. Photoluminescence spectra of a BSSC with UC-PTIR545/F embedded in the silicone with and without QDs (b).

4. Conclusion

This study reports on experimental efforts aimed at using the unique optical properties of high-quality QDs together with UC for solar cells applications.

By increasing the incident light power with an infrared LED lamp as compared to a halogen one, the UC response improves, showing a qualitative relationship between the UCs concentration in the matrix and the increase in photocurrent. The photocurrent extracted from the BSSC is found under excitation from the IR LED (1450 to 1550 nm), surely coinciding with the $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{15/2}$ Er^{3+} ions transition.

Two effective procedures for incorporating PbS into a UC have been developed. We have demonstrated that the combination of a Yb/Er-doped phosphor with PbS-QDs enhances the UC performance. To our knowledge, this is the first time this phenomenon has been experimentally shown for silicon solar cells.

Acknowledgements

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